THE REMOVAL OF ELECTRON-ELECTRON POLES FROM MANY-ELECTRON HAMILTONIANS*

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ABSTRACT

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In many-electron problems, the Hamiltonian has poles $1/r_{ij}$ which produce difficulties in the solution of the Schrodinger equation $H\psi = E\psi$. If ψ is taken to be $\phi\chi$ where $\phi = \prod_{i>j}(1 + \frac{1}{2}r_{ij})$, it is found that χ satisfies the new Schrodinger equation $H'\chi = E\chi$ where the new Hamiltonian H' has no electron-electron poles.

Author

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In many-electron problems, the Hamiltonian can usually be written in the form

$$H = \sum_{i=1}^{n} \left(-\tfrac{1}{2}\Delta_i + v_i\right) + \sum_{i>j} 1/r_{ij} \tag{1}$$

Here n is the number of electrons in the system and v_i is a function only of the coordinates of the i-th electron. The electron-electron poles corresponding to the $1/r_{ij}$ terms greatly complicate the determination of approximate wave functions. The presence of these poles might lead to spurious results if the wave function and its energy are determined by a perturbation procedure.

By the use of a correlated wave function, these poles can be removed. Let ψ be an exact eigenfunction of Schrodinger equation $H\psi = E\psi$. If $\psi = \phi\chi$, we can define a new Hamiltonian H' such that $H\psi = \phi H'\chi$. Then χ satisfies the new Schrodinger equation $H'\chi = E\chi$ with the original energy E. From Eq. (1) it follows that

$$H' = H - \tfrac{1}{2}\phi^{-1}\sum_{i=1}^{n}\left[\Delta_i\phi + 2\nabla_i\phi\cdot\nabla_i\right] \tag{2}$$

Let us take

$$\phi = \prod_{i>j} (1 + \tfrac{1}{2}r_{ij}) \quad . \tag{3}$$

The coefficient $\frac{1}{2}$ of the r_{ij} term is necessary in order to remove the poles. From (2) and (3) it follows that

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$$H' = \sum_{i=1}^{n} \left(-\tfrac{1}{2}\Delta_i + v_i\right) \tag{4}$$

$$+ \sum_{i=2}^{n} \sum_{j=1}^{i-1} (2 + r_{ij})^{-1} \left[1 - (\underset{\sim}{r}_{ij}/r_{ij}) \cdot (\nabla_i - \nabla_j) \right]$$

$$- \sum_{i=1}^{n} \sum_{k=2}^{n} \sum_{j=1}^{k-1} \frac{(\underset{\sim}{r}_{ij}/r_{ij}) \cdot (\underset{\sim}{r}_{ik}/r_{ik})}{(2 + r_{ij})(2 + r_{ik})}$$

$j, k \neq i$

Or, for two electron systems,

$$H' = -\tfrac{1}{2}(\Delta_1 + \Delta_2) + v_1 + v_2 \tag{5}$$

$$+ (2 + r_{12})^{-1} \left[1 - (\underset{\sim}{r}_{12}/r_{12}) \cdot (\nabla_1 - \nabla_2) \right]$$

In Eqs. (4) and (5), $\underset{\sim}{r}_{ij} = \underset{\sim}{r}_i - \underset{\sim}{r}_j$. The new Hamiltonian H' does not have electron-electron poles. In place of the poles occur terms involving the direction cosines $\underset{\sim}{r}_{ij}/r_{ij}$ which become discontinuous when electrons i and j come together. However, because the Pauli exclusion principle requires χ to be antisymmetric in the electrons, the term $(\underset{\sim}{r}_{ij}/r_{ij}) \cdot (\nabla_i - \nabla_j)$ becomes zero as i and j come together. Thus, $H'\chi$ is continuous for two electron systems, and for many electron systems, at worst, has a finite discontinuity. The operator H' is Hermitian with respect to suitable functions ω and Ω when ϕ^2 is used as a weight factor. Thus,

$$\int \phi^2 \omega \, H'\Omega \, d\tau = \int \phi^2 \Omega \, H'\omega \, d\tau \tag{6}$$

Examples will be considered to determine whether the Hamiltonians H' are indeed more tractable than the original H .

The idea of using a factor $(1 + c\, r_{12})$ in two electron problems is due to Hylleraas[1]. This factor has led to a very satisfactory improvement in the calculated values of the energy[2]. Generally, the value of c has been adjusted to give the optimum energy. However, only for $c = \frac{1}{2}$ is the electron-electron pole removed[3]. Other functional forms for the correlation factor have been suggested, but almost all of these forms leave the electron-electron pole intact.

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